CHARACTERIZATION OF DIESEL SOOT WITH SYNCHROTRON RADIATION TECHNIQUES

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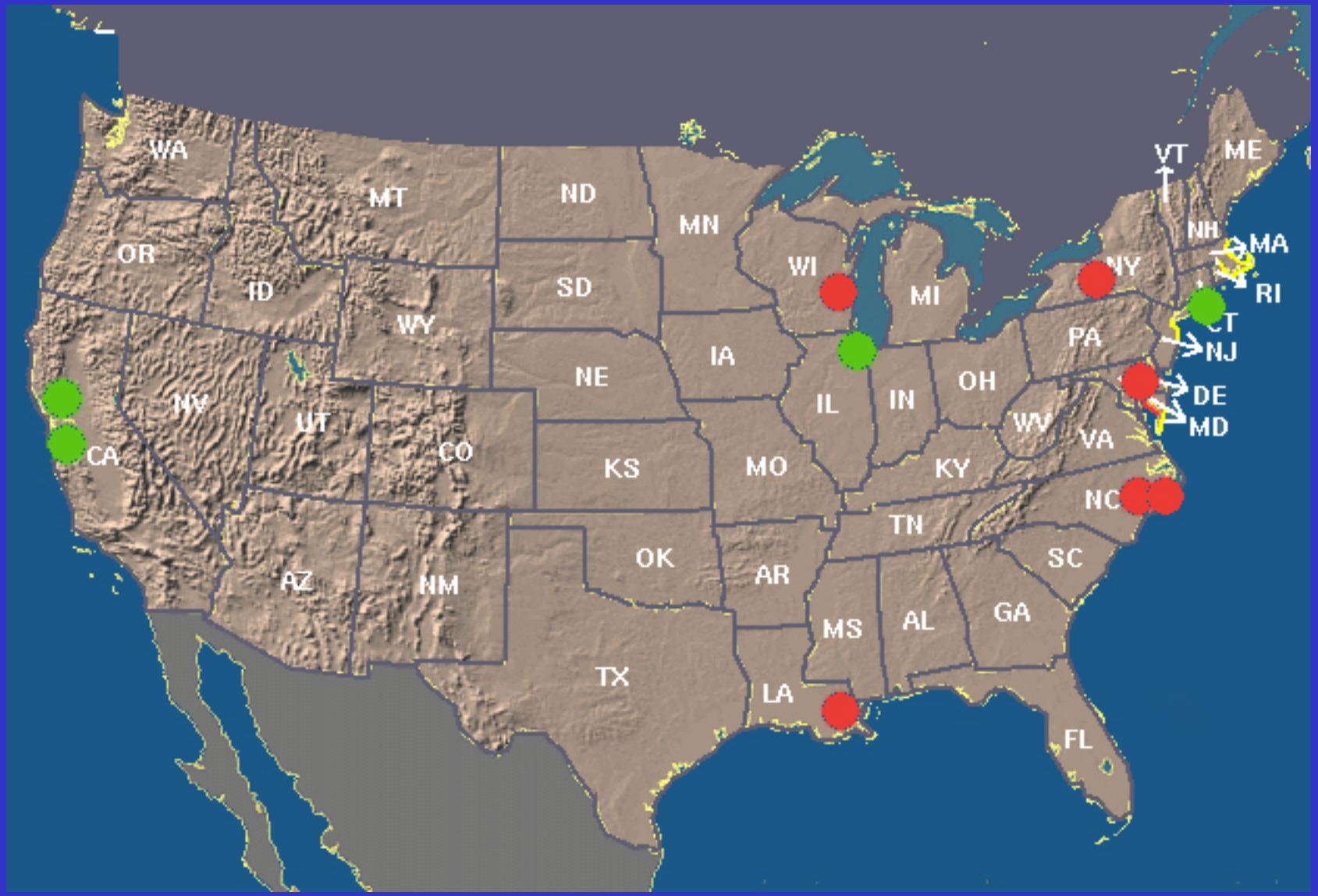
Synchrotrons

- High-intensity X-ray sources
- Available at National Labs
- Beam free of charge
- Peer reviewed system, proposal based access
- Spectroscopy, Scattering, Microscopy

Synchrotrons in the U.S.



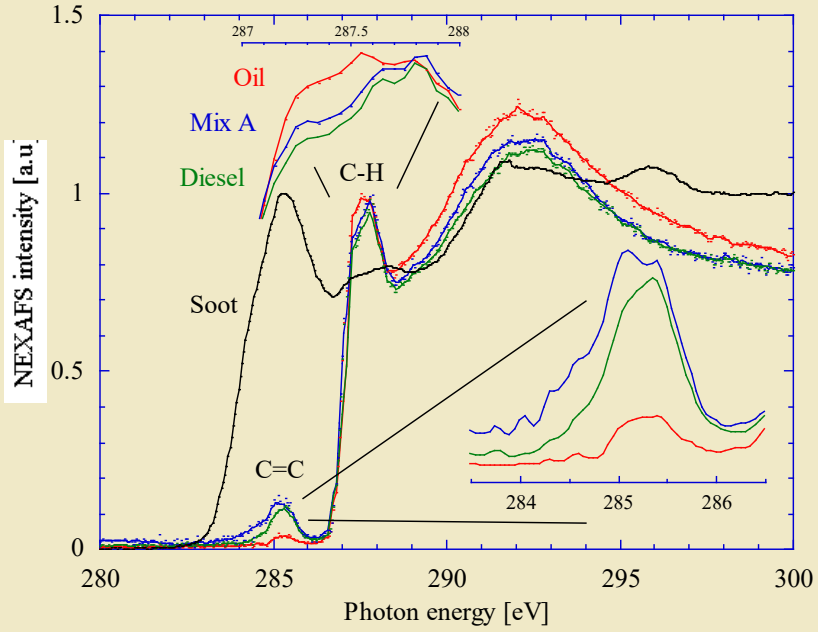
Techniques

We have used

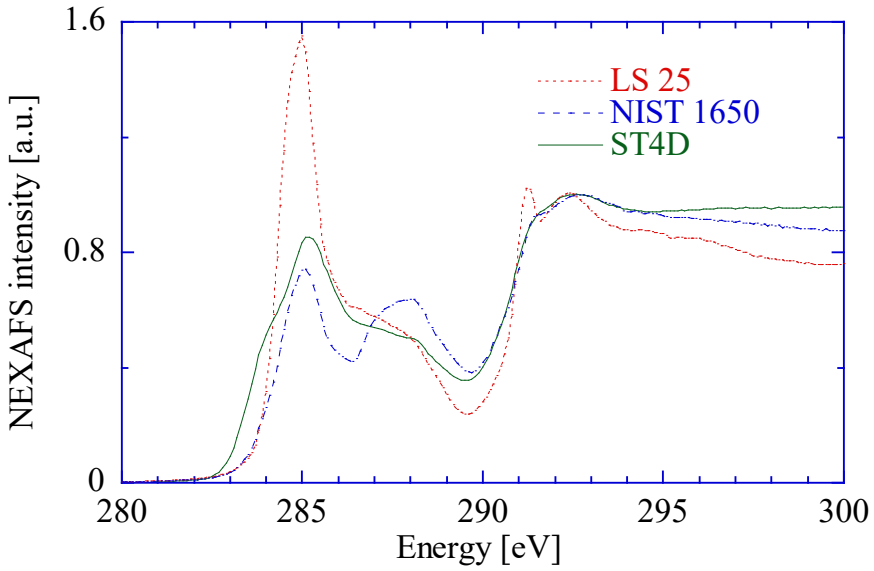
- Soft X-ray / Carbon K-edge spectroscopy (NEXAFS) for chemical characterization of organic/inorganic carbon in soot
- Wide angle X-ray scattering for microstructure analysis
- Small angle X-ray scattering for microstructure analysis
- a combination of microscopy and spectroscopy (STXM)

NEXAFS

Near-edge X-ray Absorption Fine Structure Spectroscopy



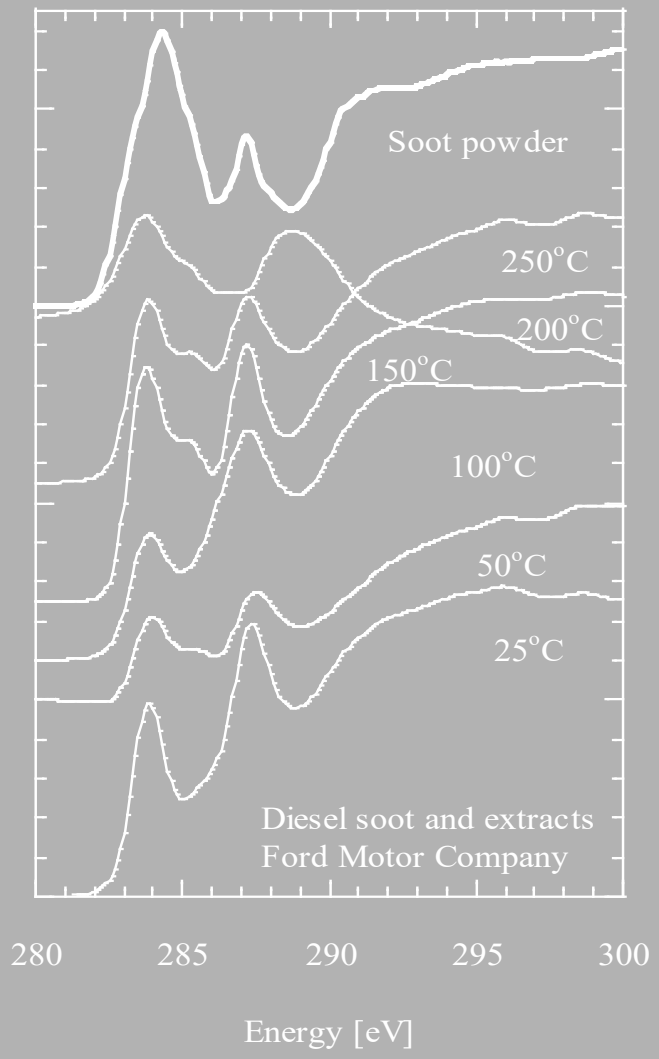
Allows for chemical speciation of samples, and determination of oxidation states.



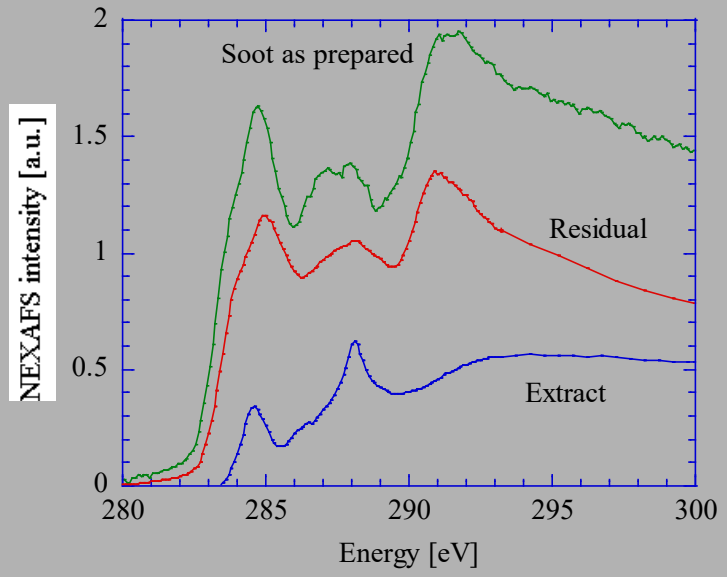
Spectra of soot, lubricant, fuel.

Graphite, diesel soot, ethylene soot

Soot Extracts

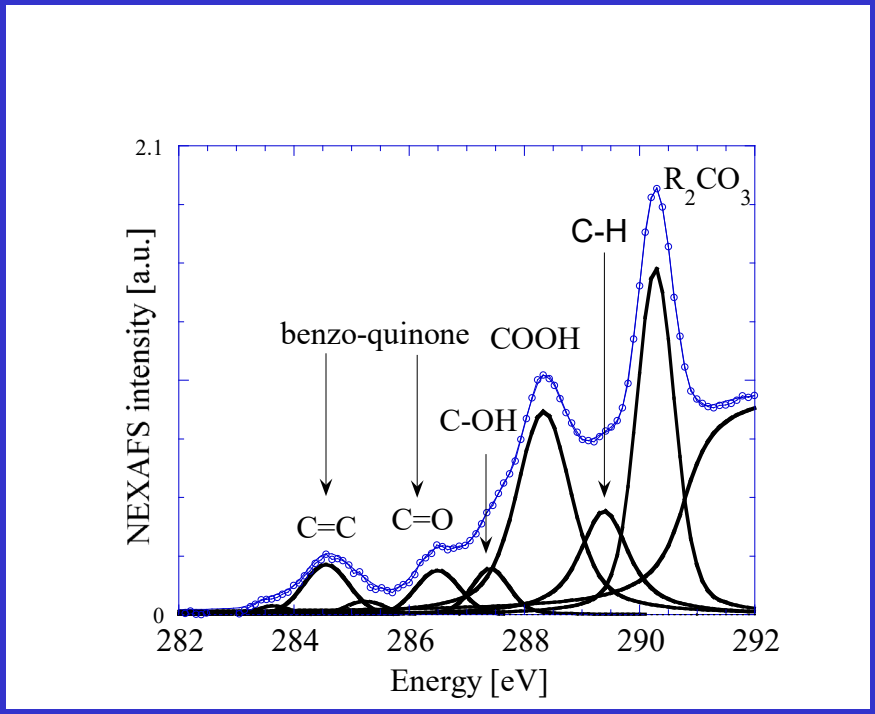


Separation of diesel soot into solid core and volatile fractions with subcritical water facilitates subsequent decomposition of NEXAFS spectra.



A. Kubatove et al. ENVIRONMENTAL TOXICOLOGY AND CHEMISTRY 23 (9): 2243-2250 SEP 2004

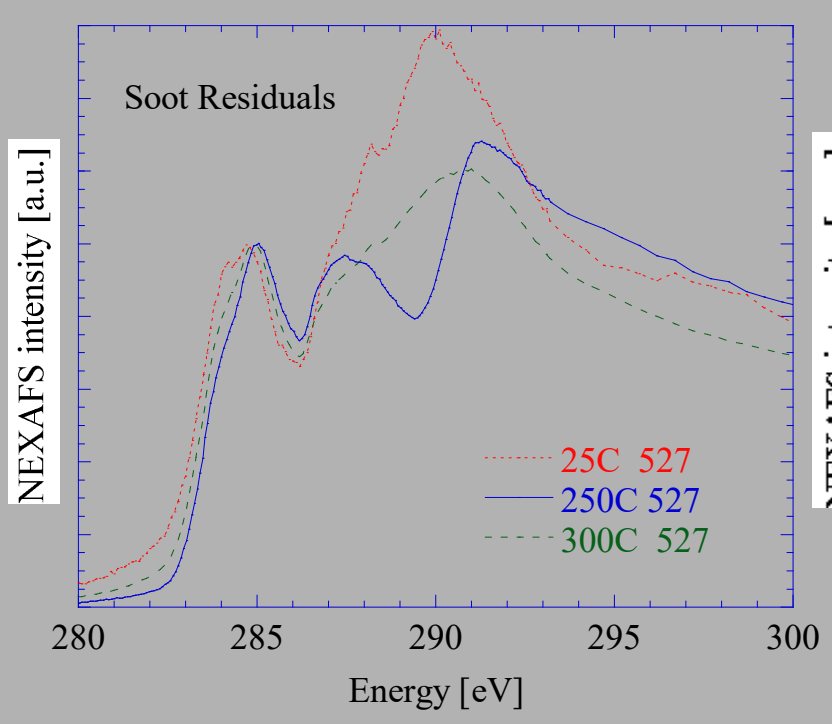
NEXAFS Peak Assignments of Soot Extracts

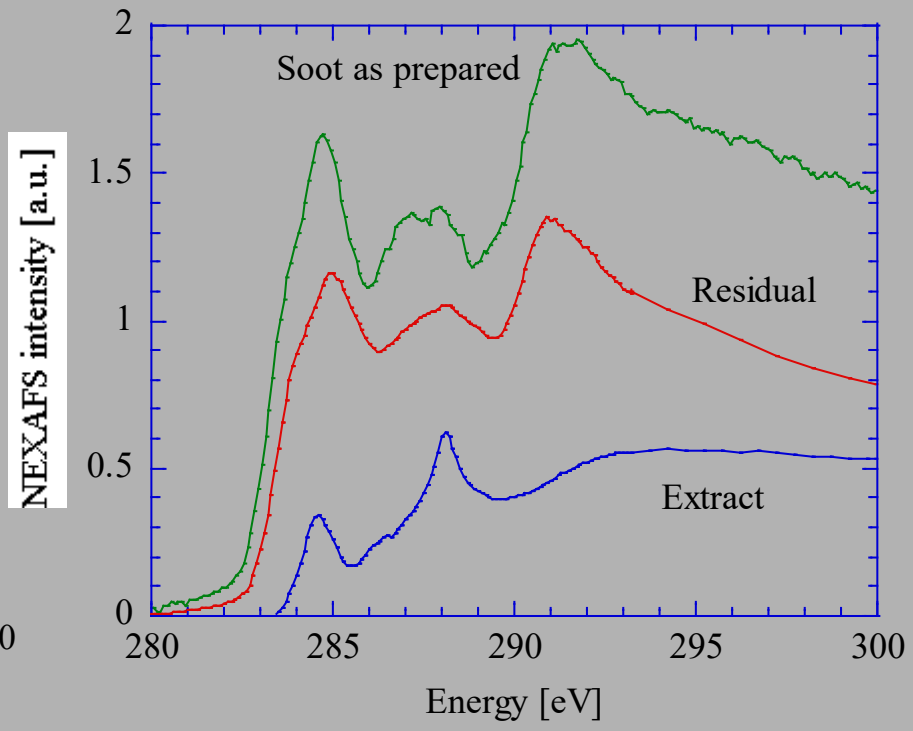


Potential tool for in-situ reaction studies !

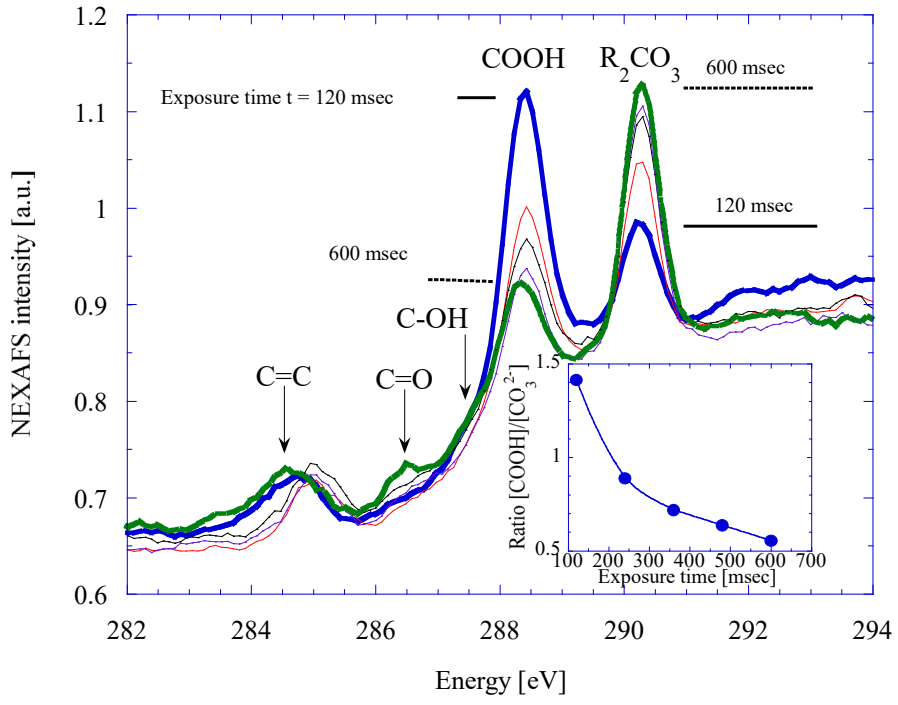
Soot Residual

Separation of diesel soot into solid core and volatile fractions with subcritical water facilitates subsequent decomposition of NEXAFS spectra.





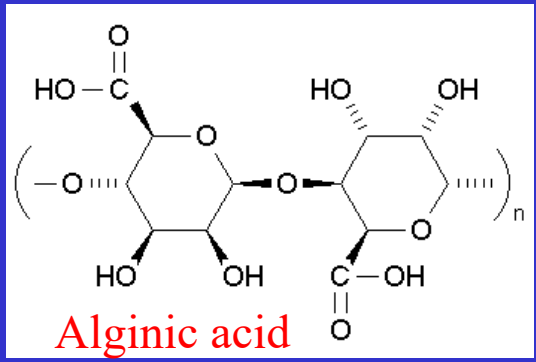
Soot Extracts – Interaction With Oxygen



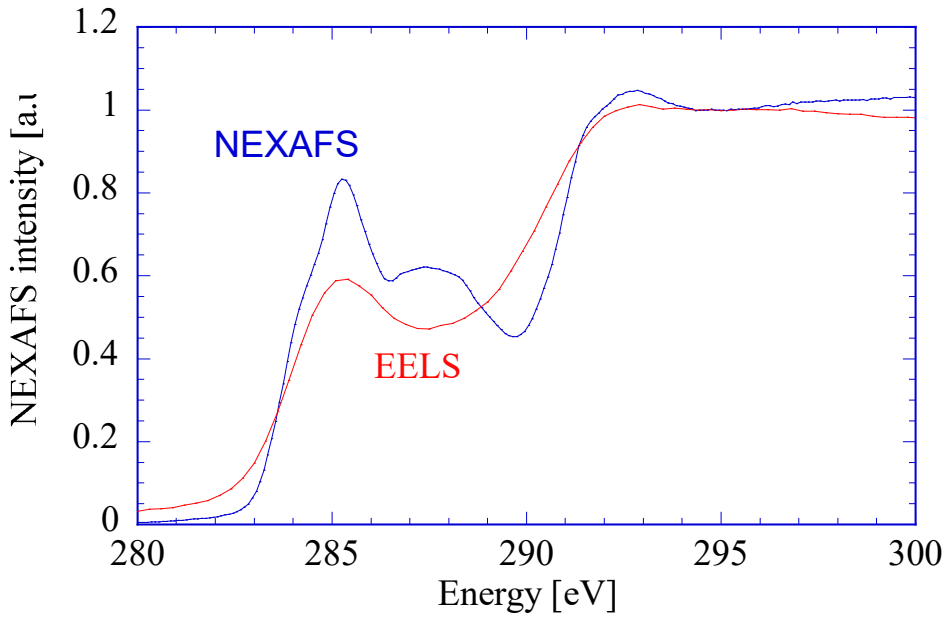
Intense X-ray beam of the STXM microscope generates nascent oxygen from air.

Upon irradiation,COOH carboxyl peak intensity decreases, and new peak evolves - probably from organo-carbonate.

Potential tool for in-situ reaction studies !



NEXAFS vs. EELS

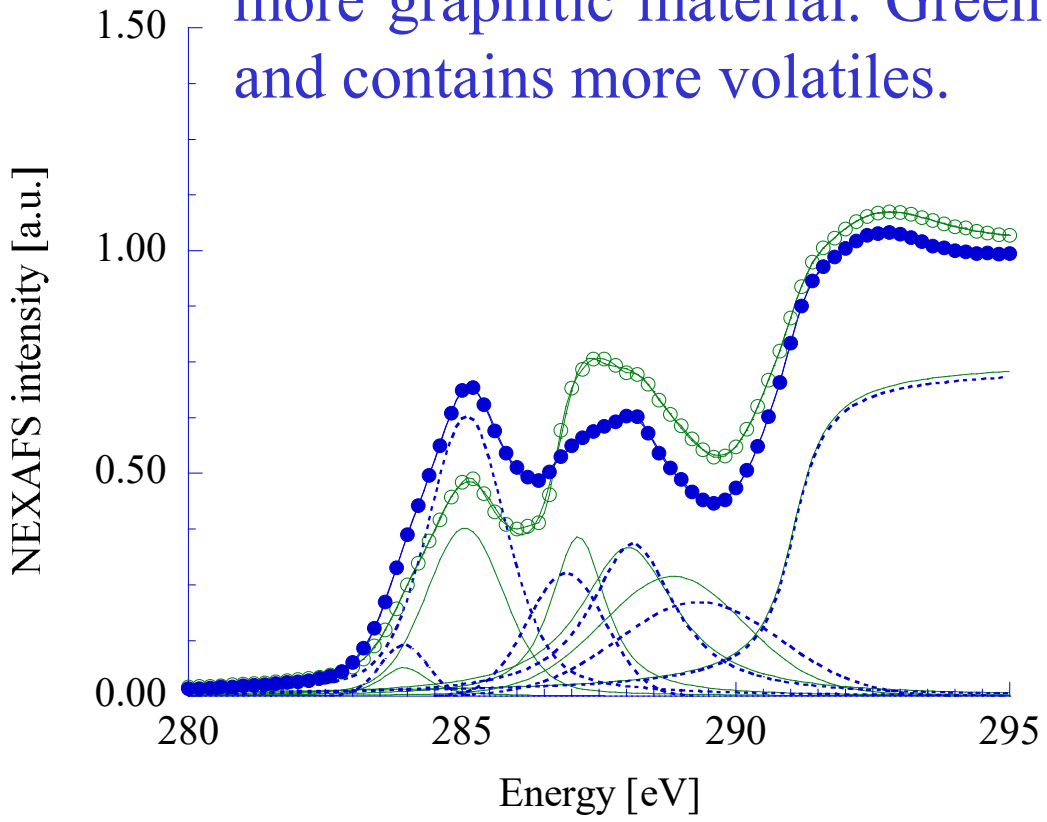


EELS and NEXAFS have similar spectra. TEM microscopes often come with an EELS spectrometer. But EELS spectra from TEM look blurred, almost entirely useless for quantitative studies.

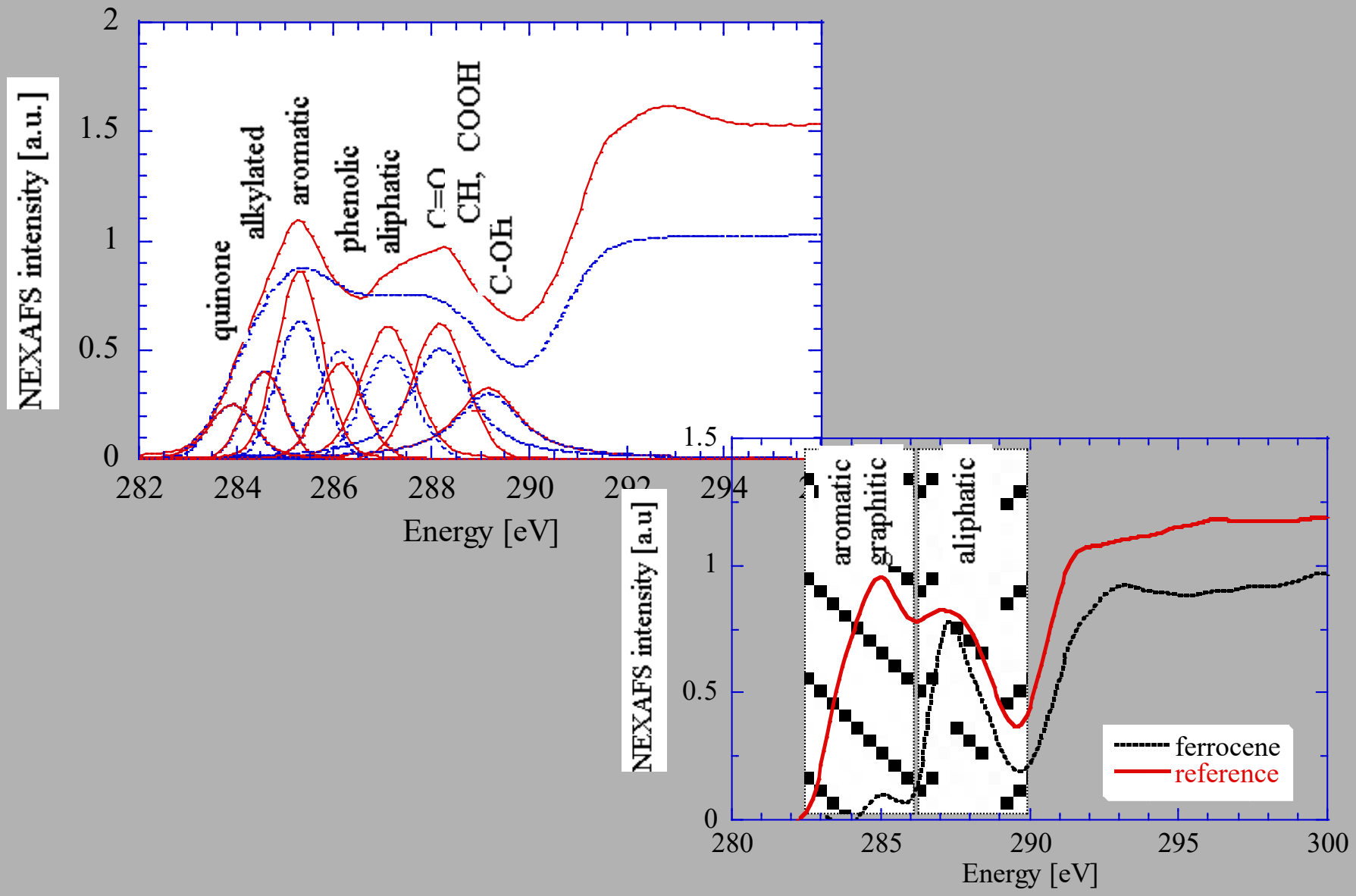
Advantages of soft X-ray absorption over TEM-EELS - A Comparative studies on diesel soot with EELS and NEXAFS, CARBON, in press

NEXAFS of Idle and Load Soot

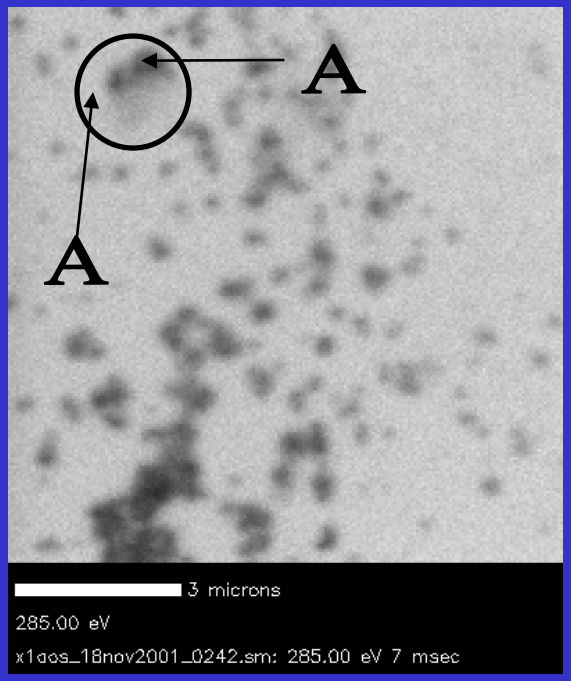
NEXAFS spectra of soot from **idle** or load condition look different, and permit for quantitative analysis of constituents. Blue spectrum is from load soot and contains more graphitic material. Green spectrum is from **idle** soot and contains more volatiles.

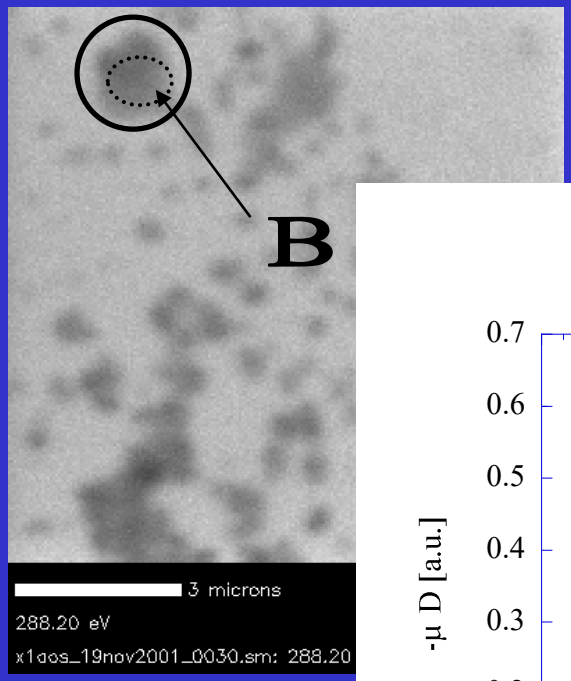


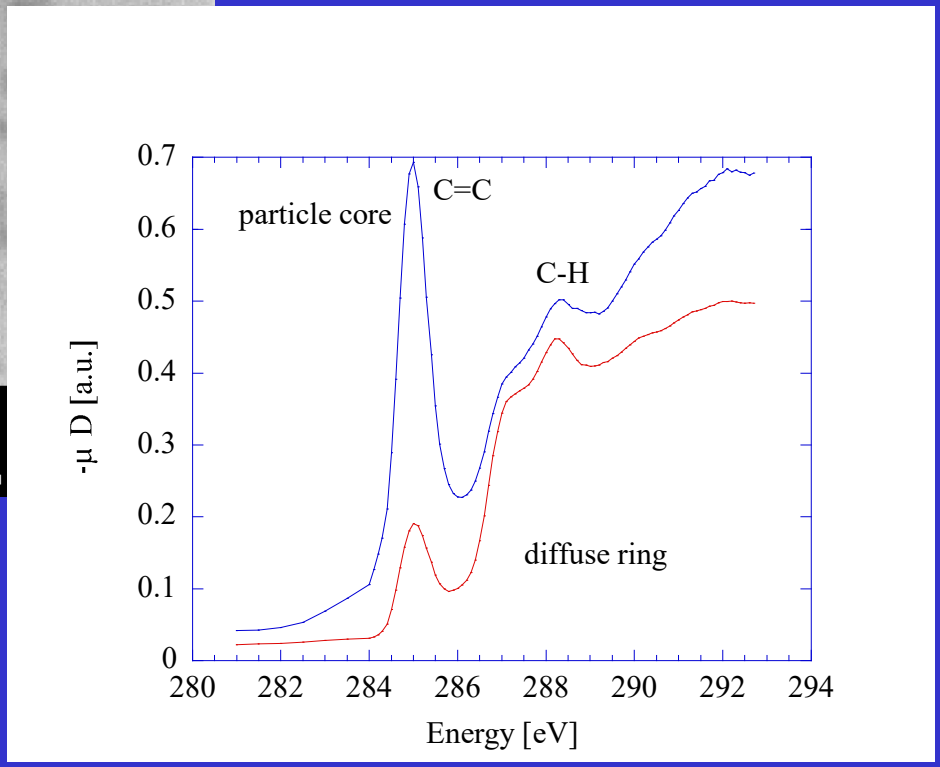
Idle/load, and ferrocene doped fuel soot



Scanning Transmission X-ray Microspectroscopy





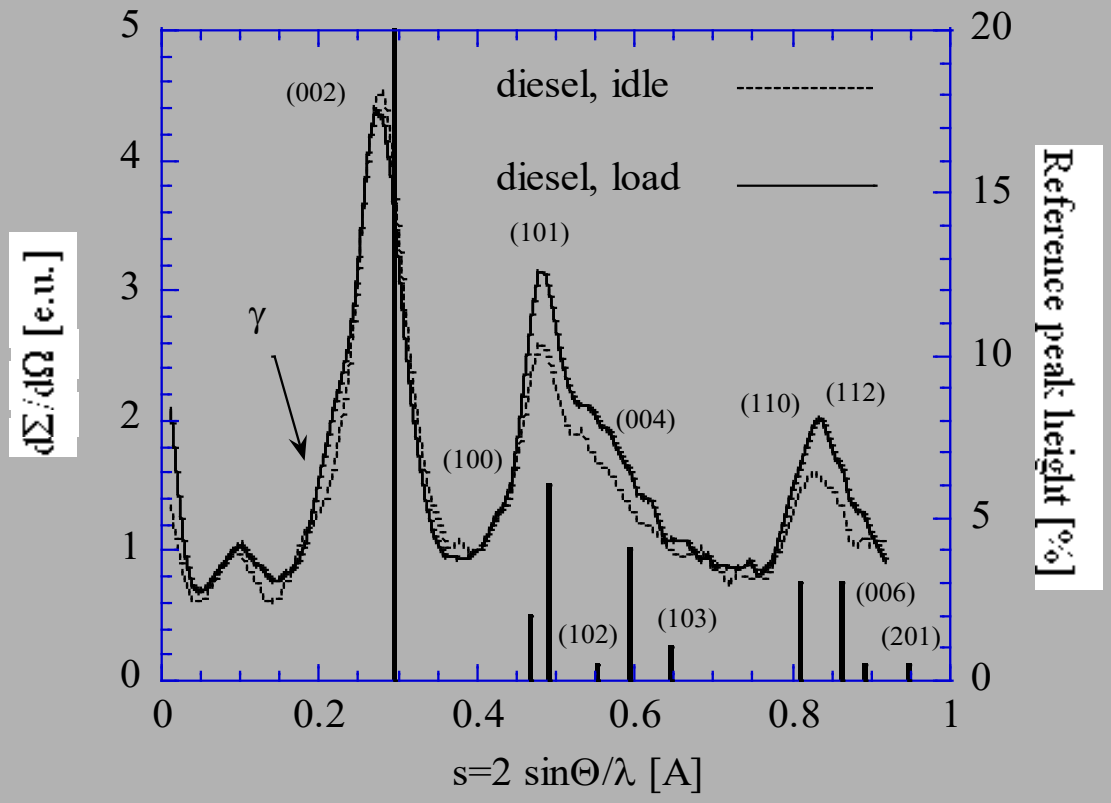


STXM is X-ray microscopy with chemical contrast of 0.1 eV resolution

Study of fine diesel particulate matter with scanning transmission X-ray spectroscopy. Fuel 2004 10 7/8 997-1000.

WAXS - Wide-angle X-ray Scattering

Similar to X-ray diffraction, but diffuse scattering.
No crystallography, but information on microsctructure.

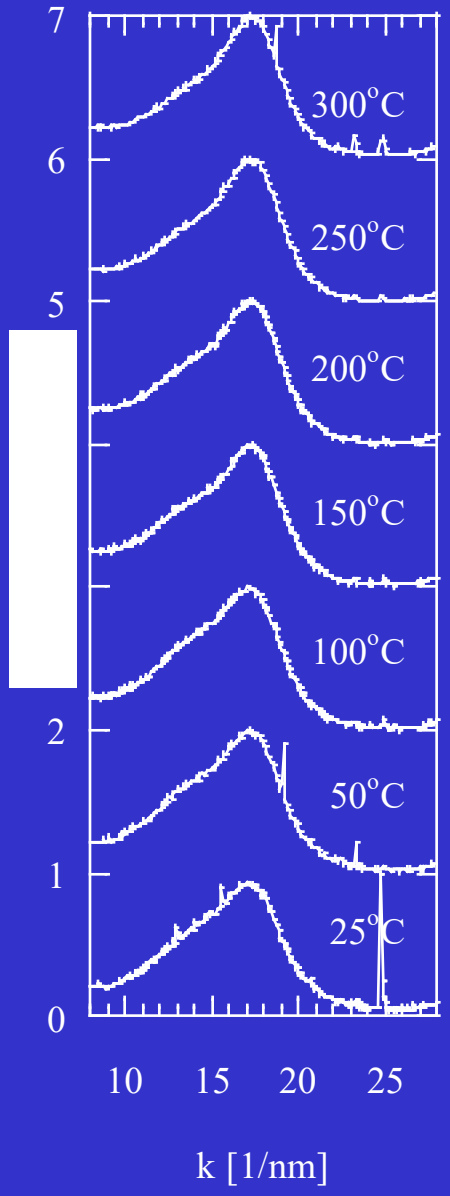


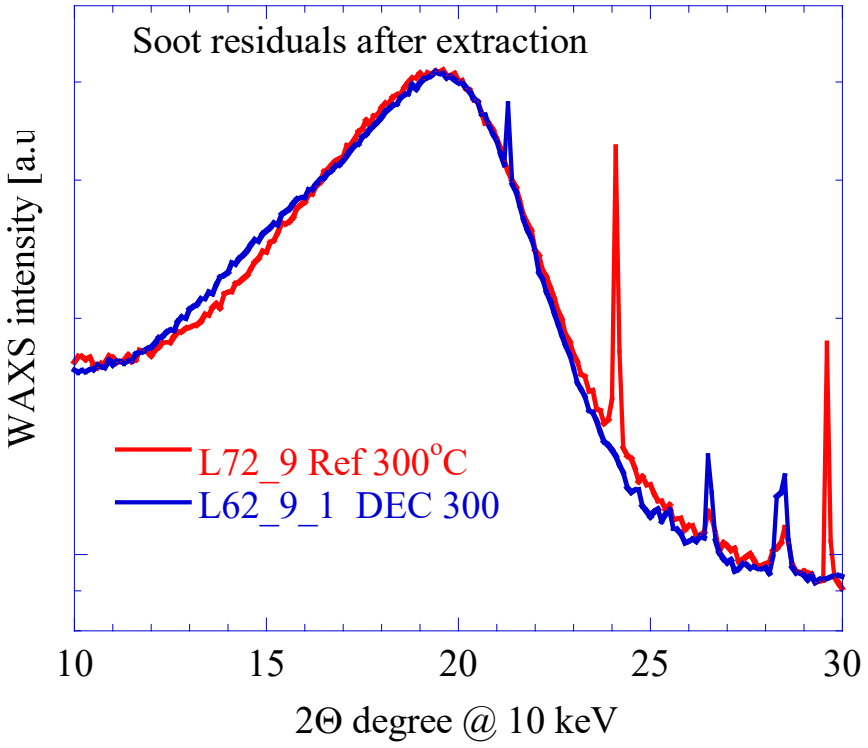
X-ray diffractograms of Idle and load diesel soot. Recorded with a Siemens diffractometer.

In WAXS, profiles of low-indexed peaks are important.

WAXS

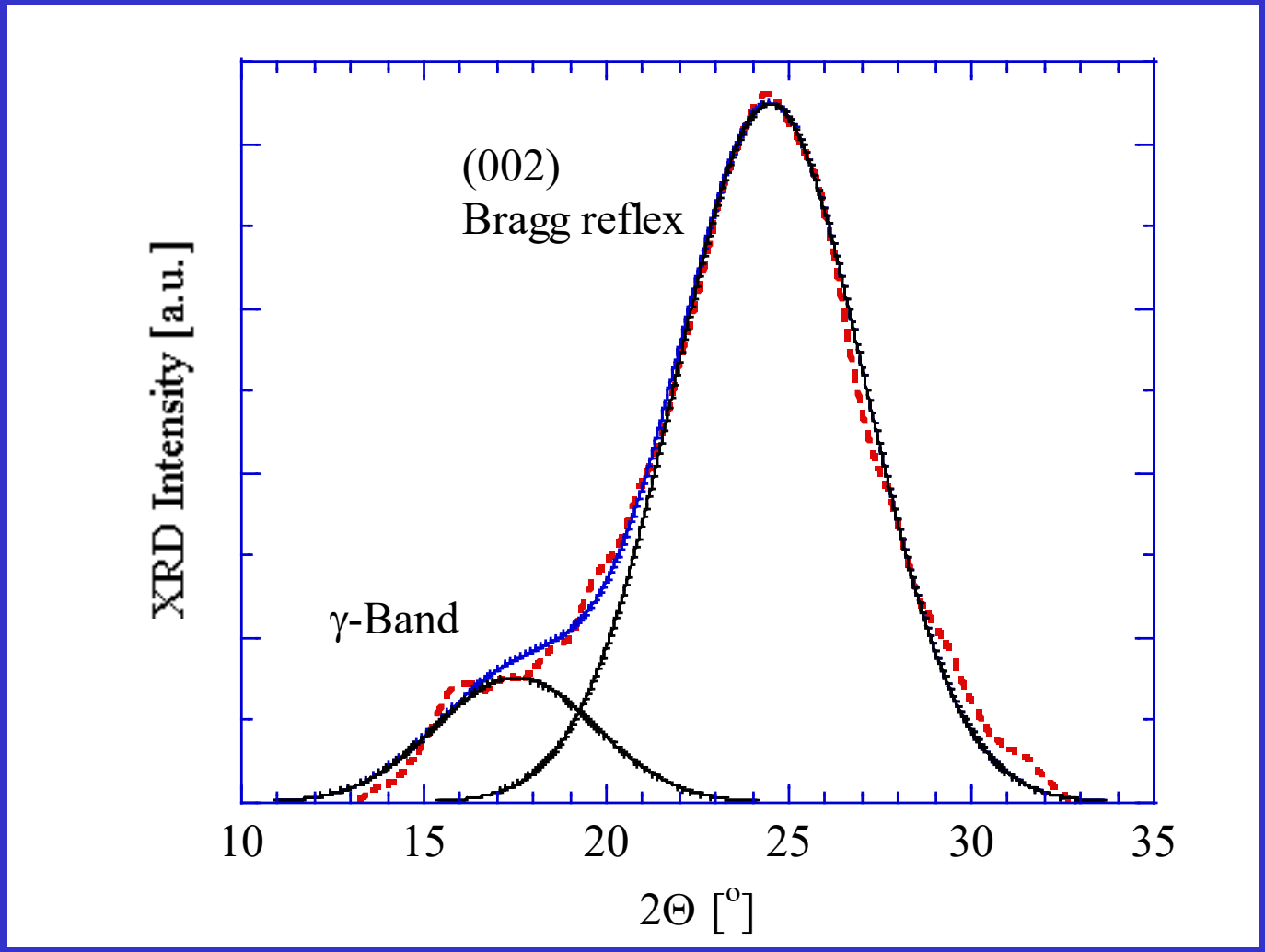
WAXS data of soot residuals from DEC treated diesel fuel. Temperatures denote the extraction temperature.





Deconvolution of (002) Reflex

(002) Bragg reflex accompanied by aliphatic side band



Structure parameters from WAXS

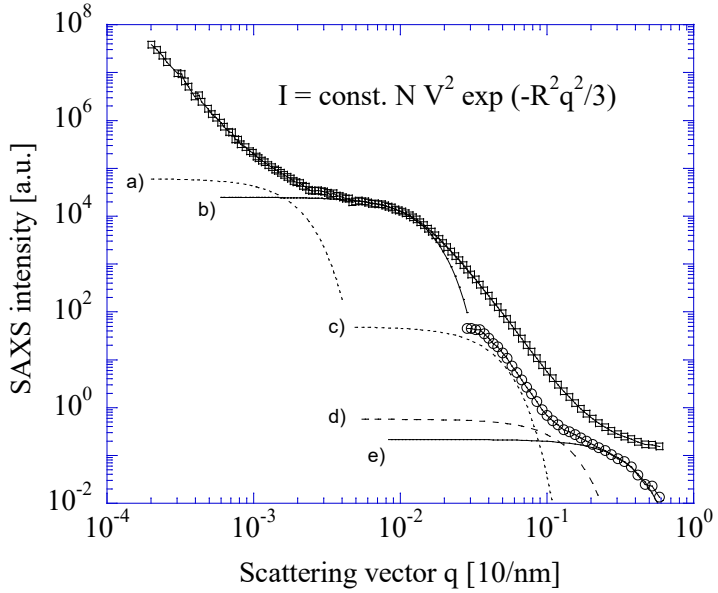
	Aromaticity *f* of diesel soot		
fuel	diesel	diesel Mix A	diesel Mix B
idle	0.152	0.342	0.307
load	0.218	0.152	0.075

Sample	L_c (002) [Å]	L_a (110) [Å]	L_a (112) [Å]
Diesel, idle	11.10	8.67	17.24
Diesel, load	11.78	10.48	16.68
Mix B, idle	10.18	6.96	13.24
Mix B, load	12.86	8.64	14.92
Mix A, idle	8.64	8.93	6.24
Mix A, load	10.78	16.30	11.19

(U-)SAXS

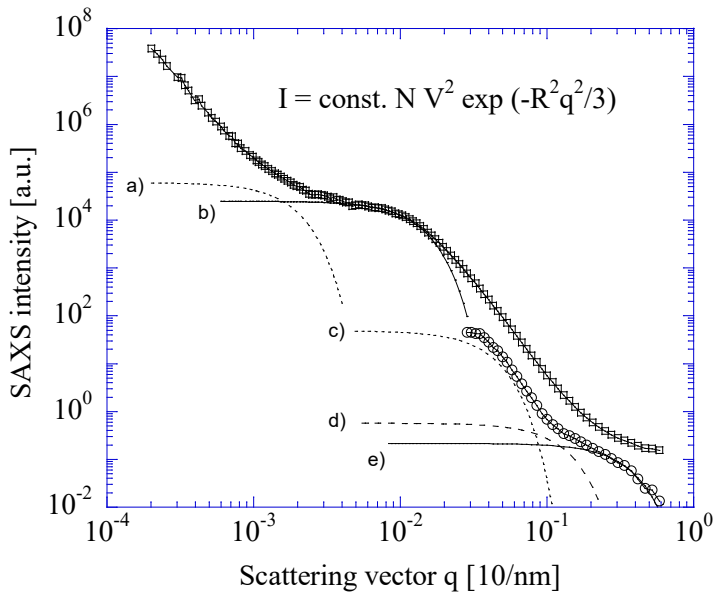
(Ultra-) Small angle X-ray Scattering

Technique for particle size determination, fractal dimension, surface area, porosity, etc. Similar to XRD/WAXS, but diffuse scattering. Investigates the (0,0) Bragg reflex / specular beam.



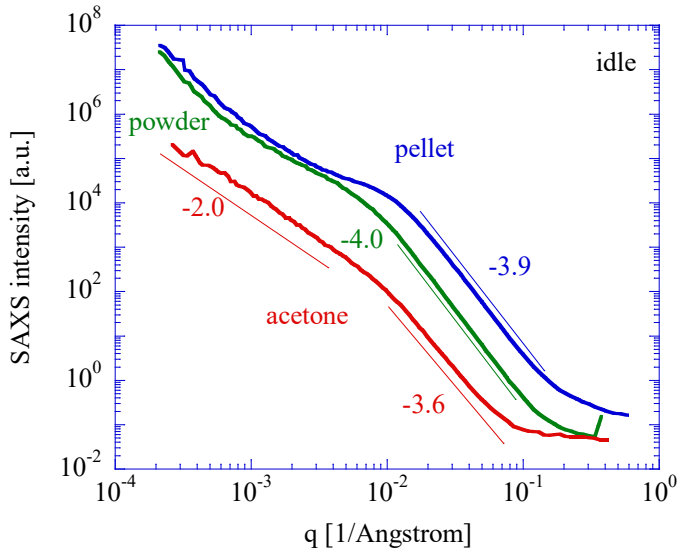
Size-range analysis of diesel soot with ultra small angle X-ray scattering. Combustion & Flame (2004) **137** 1-2 pp. 63-72.

Particle sizes



Soot	Elementary units D [nm]	Subunits D [nm]	Primary particles D [nm]
Diesel, idle	1.5	17.4	49.16
Diesel, load	1.6	14.5	41.50
Mix A, idle	1.9	21.1 (14.2)	78.29
Mix A, load	1.4	13.8 (12)	36.78
Mix B, idle	2.0	14.3 (14.5)	83.85
Mix B, load	1.4	22.0 (18.6)	48.73

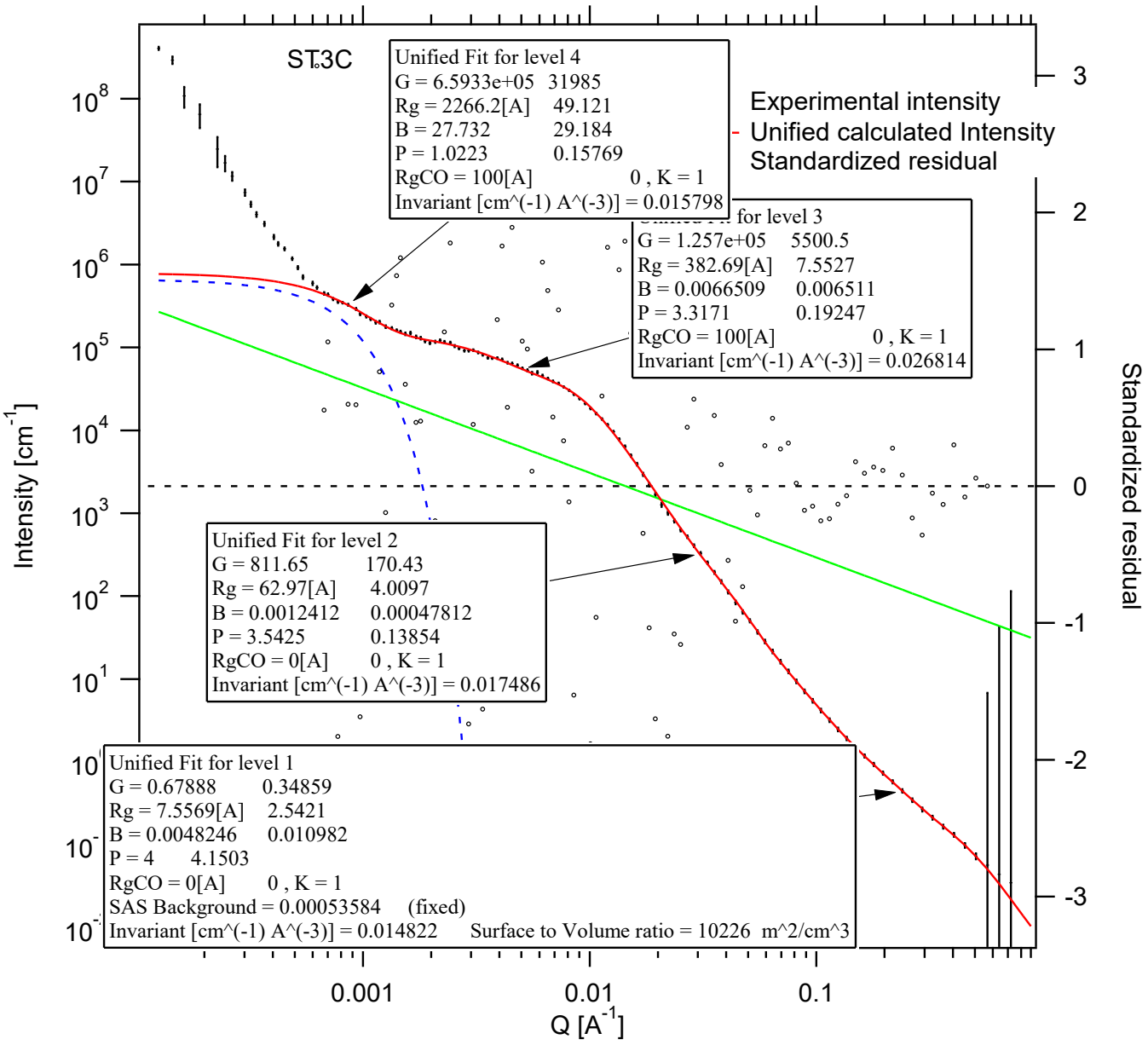
Fractal dimension



Slope of straight segments in SAXS curves tells the fractal dimension.

Soot	high q exponent	Fractal dimension	low q exponent	Fractal dimension
Diesel, idle	3.99	2.01	3.28	2.72
Diesel, load	3.86	2.14	3.12	2.88
Mix A, idle	3.97	2.03	3.02	2.98
Mix A, load	3.96	2.04	3.09	2.91
Mix B, idle	3.92	2.08	2.96	2.96
Mix B, load	3.98	2.02	2.75	2.75

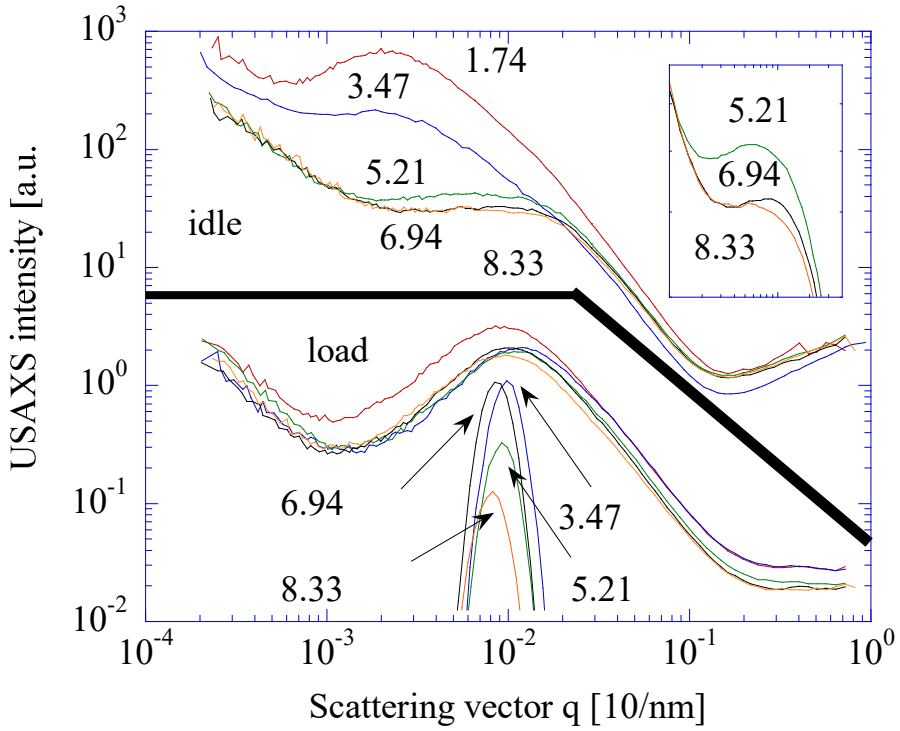
Modelling of USAXS Curves



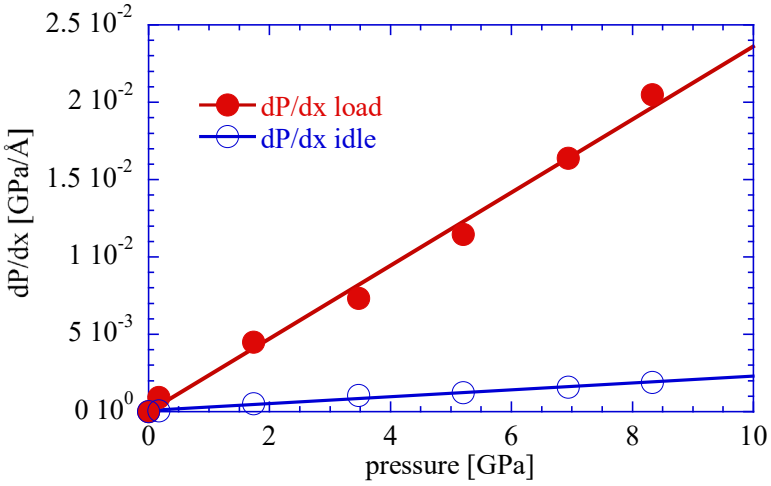
Modelling of USAXS Curves

	Rg	n	Rg	n	Rg	n	Rg	n
ST3C	7.5569	4	62.97	3.5425	382.69	3.3171	2266.2	1
ST4D	7.3307	4	54.864	3.5271	420.55	3.4342	1783.3	1
ST5E	11.565	1.9899	89.185	3.8188	385.84	4.1866	1388.2	1

USAXS for different pellet pressure



Pressure dependence of USAXS from soot pellets is different for load and idle condition.



USAXS for different pellet pressure